



US009101093B2

(12) **United States Patent**
Chance et al.

(10) **Patent No.:** **US 9,101,093 B2**
(45) **Date of Patent:** **Aug. 11, 2015**

(54) **WATER/CARBONATE STRIPPING FOR CO₂ CAPTURE ADSORBER REGENERATION AND CO₂ DELIVERY TO PHOTOAUTOTROPHS**

(75) Inventors: **Ronald Chance**, Naples, FL (US);
William J. Koros, Atlanta, GA (US);
Benjamin McCool, Bonita Springs, FL (US); **James Noel**, Atlanta, GA (US)

(73) Assignees: **Algenol Biotech LLC**, Fort Myers, FL (US); **Georgia Tech Research Corp.**, Atlanta, GA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 418 days.

(21) Appl. No.: **13/417,172**

(22) Filed: **Mar. 9, 2012**

(65) **Prior Publication Data**

US 2012/0171752 A1 Jul. 5, 2012

Related U.S. Application Data

(63) Continuation-in-part of application No. PCT/US2010/059684, filed on Dec. 9, 2010.

(60) Provisional application No. 61/267,968, filed on Dec. 9, 2009.

(51) **Int. Cl.**
B01D 53/02 (2006.01)
A01G 7/02 (2006.01)

(52) **U.S. Cl.**
CPC **A01G 7/02** (2013.01)

(58) **Field of Classification Search**
CPC **A01G 7/02**
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

7,699,909 B2	4/2010	Lackner et al.
7,708,806 B2	5/2010	Wright et al.
2006/0266217 A1	11/2006	Jensvold
2007/0022877 A1	2/2007	Marand et al.

(Continued)

FOREIGN PATENT DOCUMENTS

EP	PCT/EP2009/000892	8/2009
WO	WO2008042919	10/2008
WO	WO2011072122	6/2011

OTHER PUBLICATIONS

U.S. Appl. No. 61/267,968, filed Dec. 9, 2009.

(Continued)

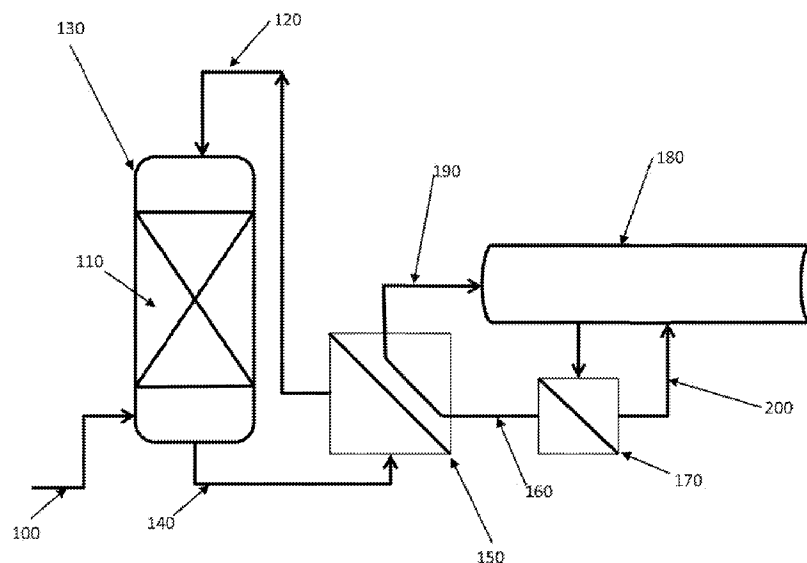
Primary Examiner — Christopher P Jones

(74) *Attorney, Agent, or Firm* — Lawrence B. Ebert; David J. Lorenz

(57) **ABSTRACT**

The invention provides systems and methods for the delivery of carbon to photoautotrophs. The invention utilizes low energy regeneration of adsorbent for CO₂ capture and provides for effective CO₂ loading into liquids useful for photoautotroph growth and/or production of photosynthetic products, such as biofuels, via photoautotrophic culture media. The inventive system comprises a fluid/membrane/fluid contactor that provides selective transfer of molecular CO₂ via a dense (non-porous) membrane from a carbonate-based CO₂ stripping solution to a culture medium where the CO₂ is consumed by a photoautotroph for the production of biofuels, biofuel precursors or other commercial products.

17 Claims, 15 Drawing Sheets



(56)

References Cited**U.S. PATENT DOCUMENTS**

2008/0087165	A1	4/2008	Wright et al.	
2008/0138265	A1	6/2008	Lackner et al.	
2009/0120288	A1	5/2009	Lackner et al.	
2009/0232861	A1	9/2009	Wright et al.	
2012/0107792	A1*	5/2012	Babbitt et al.	435/3

OTHER PUBLICATIONS

Ball, "Eukaryotic Microalgae Genomics: The Essence of Being a Plant," *Plant Physiology* 137: 397-398 (2005).

Koros et al., "Technology for Membranes and Membrane Processes (IUPAC Recommendations 1996)," *Pure and Applied Chemistry*, vol. 68, pp. 1479-1489 (1996).

Green et al., *Chemical Engineers' Handbook*, Eighth Edition, ISBN: 0071422943, p. 17-18.

K. Sato et al., "Development of practically available up-scaled high-silica CHA-type zeolite membranes for industrial purpose in dehydration of N-methyl pyrrolidone solution", *Journal of Membrane Science* 409-410 (2012) 82-95.

Meille et al., "Definitions Of Terms Relating To Crystalline Polymers (IUPAC Recommendations 2011)", *Pure and Applied Chemistry*, vol. 83, pp. 1831-1871 (2011).

McGraw-Hill Dictionary of Architecture and Construction (2003), p. 359.

Kim et al., "Enthalpy of absorption of CO₂ with alkanolamine solutions predicted from reaction equilibrium constants," *Chemical Engineering Science*, 64(9): 2027 (2009).

Kim et al., "Heat of absorption of carbon dioxide (CO₂) in monoethanolamine (MEA) and 2-(aminoethyl) ethanolamine (AEEA) solutions, *Industrial & Engineering Chemistry Research*," 46 (2007), pp. 5803.

Belmabkhout et al., "Adsorption" (2009) 15: pp. 318-328.

Green et al., *Chemical Engineers' Handbook*, Eighth Edition, ISBN: 0071422943, p. 17-18 (2007).

Luo et al., Life Cycle Energy and Greenhouse Gas Emissions for an Ethanol Production Process Based on Blue-Green Algae. *Environmental Science & Technology* 2010, 44, (22), 8670-8677.

Solomon et al., IPCC 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.

Noel et al., Membrane-Mediated Delivery of Carbon Dioxide for Consumption by Photoautotrophs: Eliminating Thermal Regeneration in Carbon Capture, *Ind. Eng. Chem. Res.* 2012, 51, 4673-4681.

Treut et al., Historical Overview of Climate Change. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Knuutila, H. et al., "CO₂ capture from coal-fired power plants based on sodium carbonate slurry; a systems feasibility and sensitivity study," *International Journal of Greenhouse Gas Control* 3 (2009) pp. 143-151.

Felder and Rousseau, "Principles of Chemical Processes," 3rd Ed., John Wiley and Sons (2005).

Lee, L.L., "Thermodynamic models for natural gas sweetening fluids," Report on GPI/GPA Project 5091-260-2288, University of Oklahoma, Norman, OK, USA (1996) p. 216.

Lee, L.L., "Thermodynamic models for natural gas sweetening fluids," Annual Report, GRI Contract No. 5091-260-2288, University of Oklahoma, Norman, OK, USA (1994).

* cited by examiner

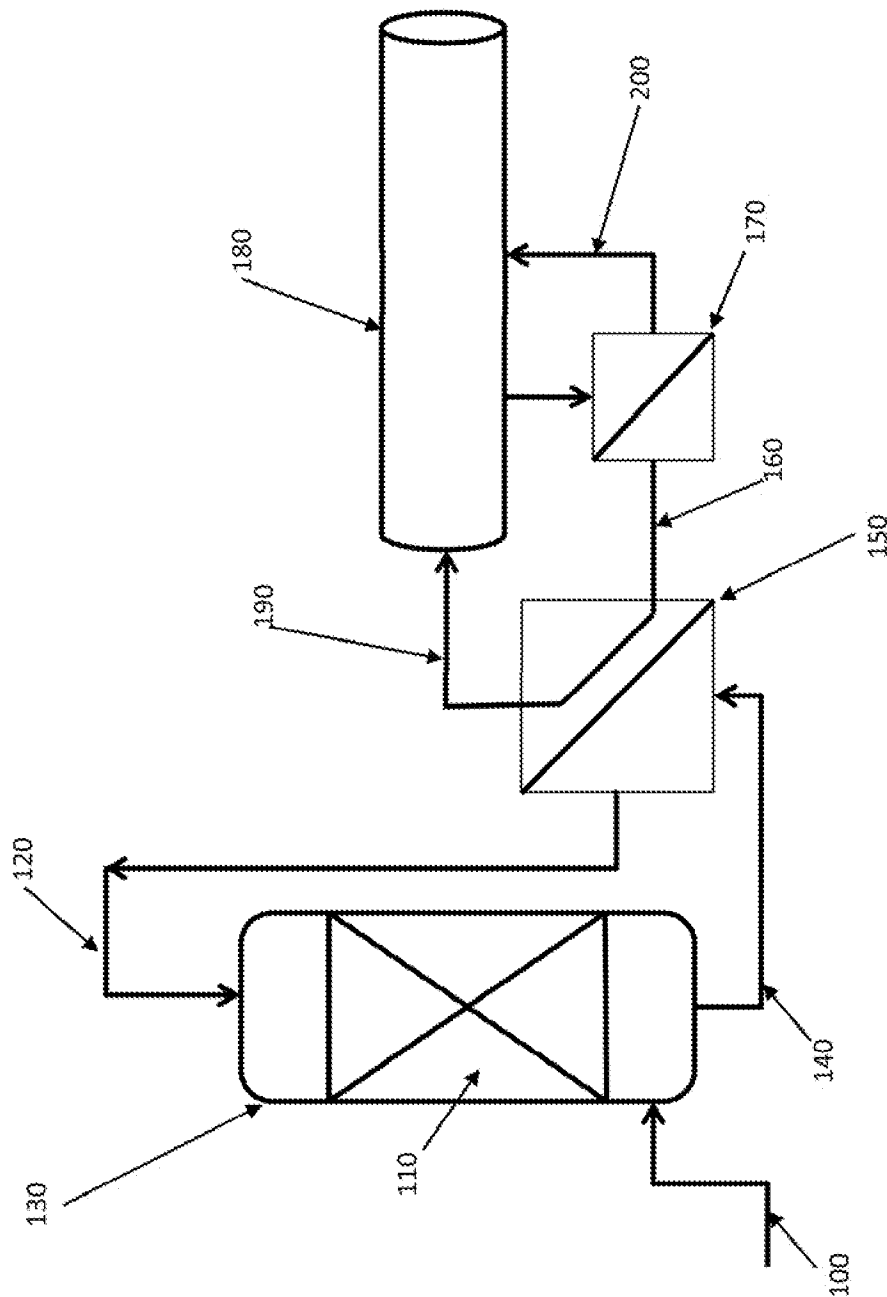


Fig. 1

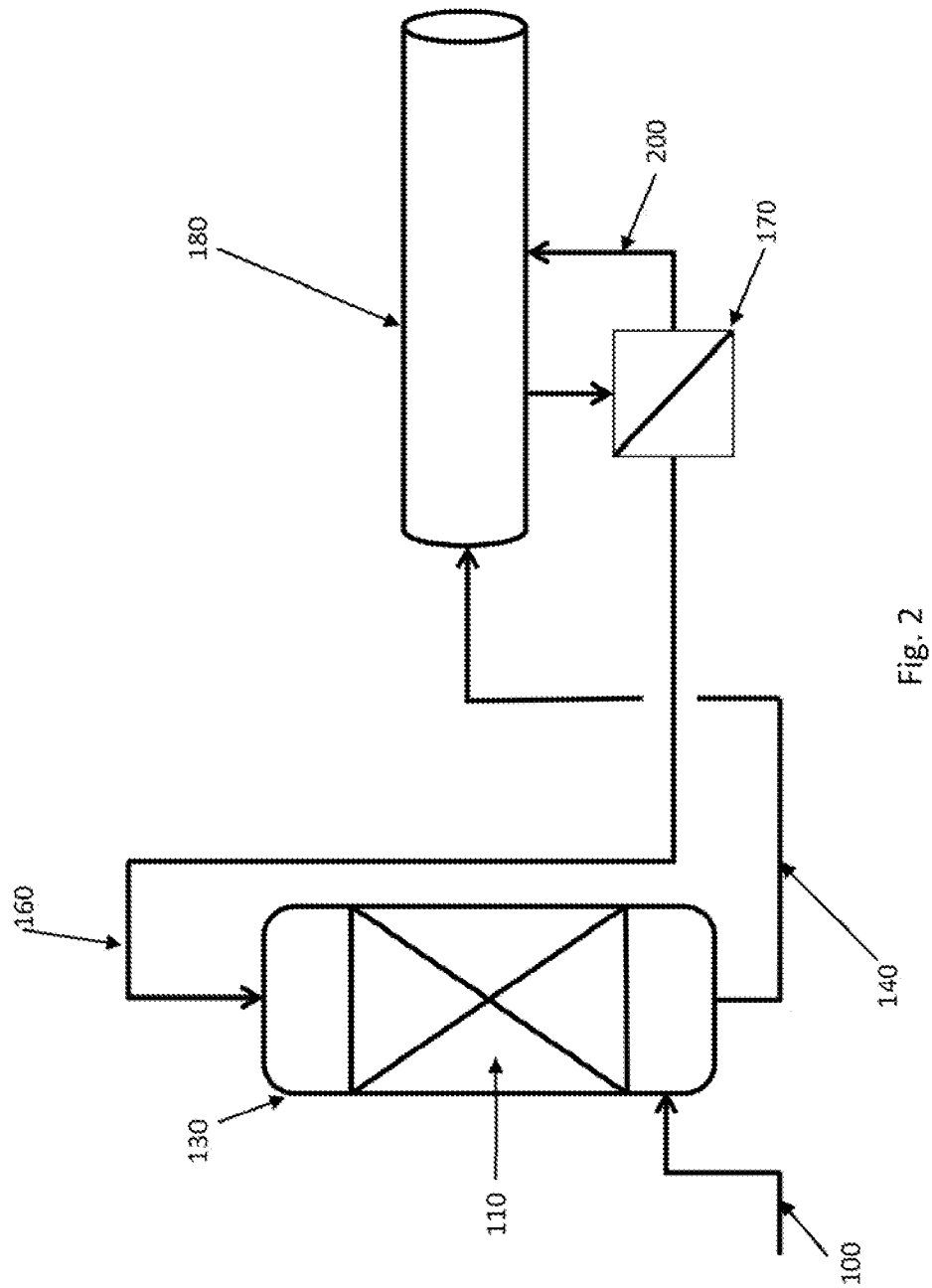


Fig. 2

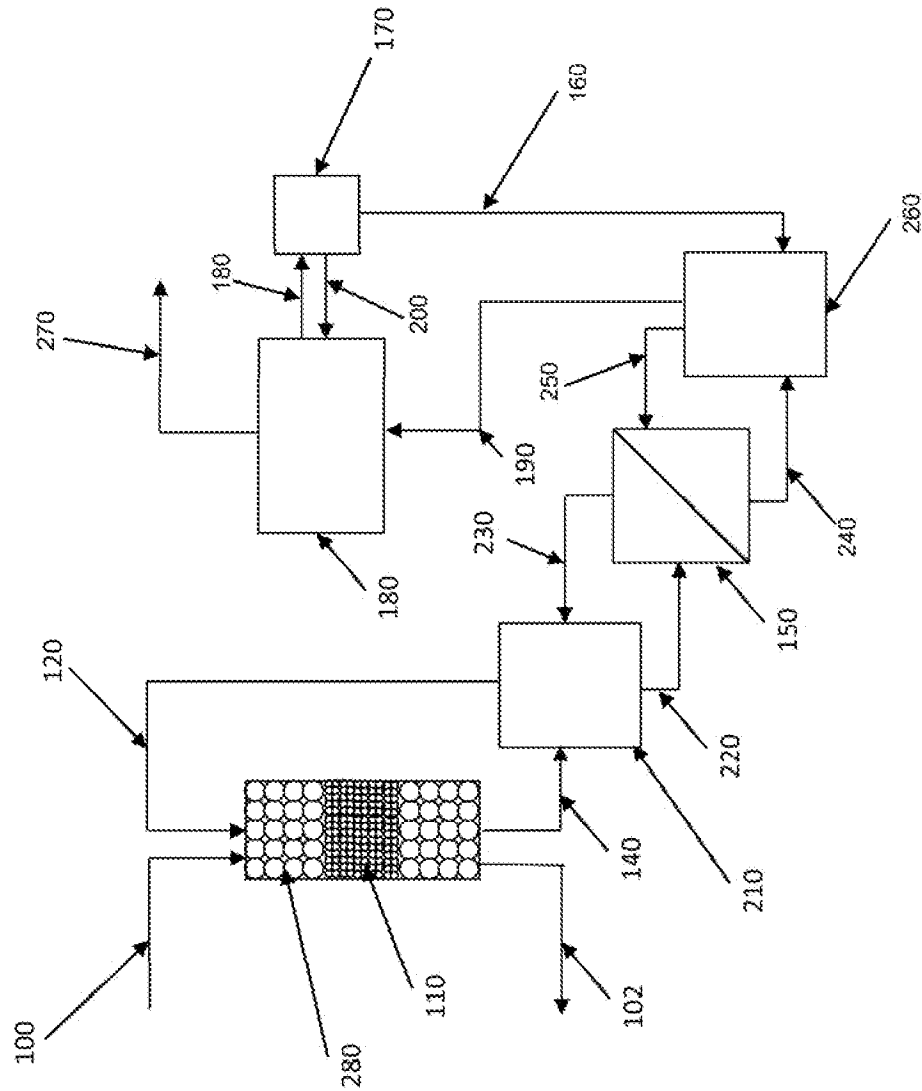


Fig. 3

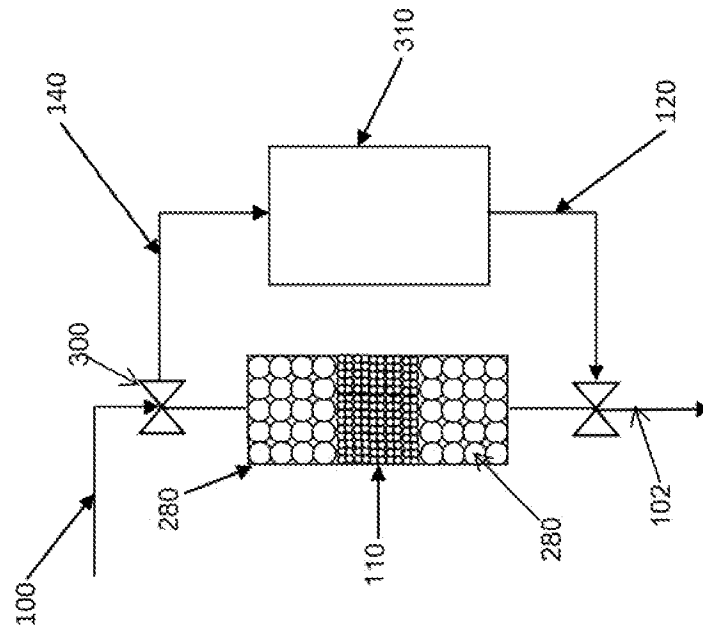


Fig. 4

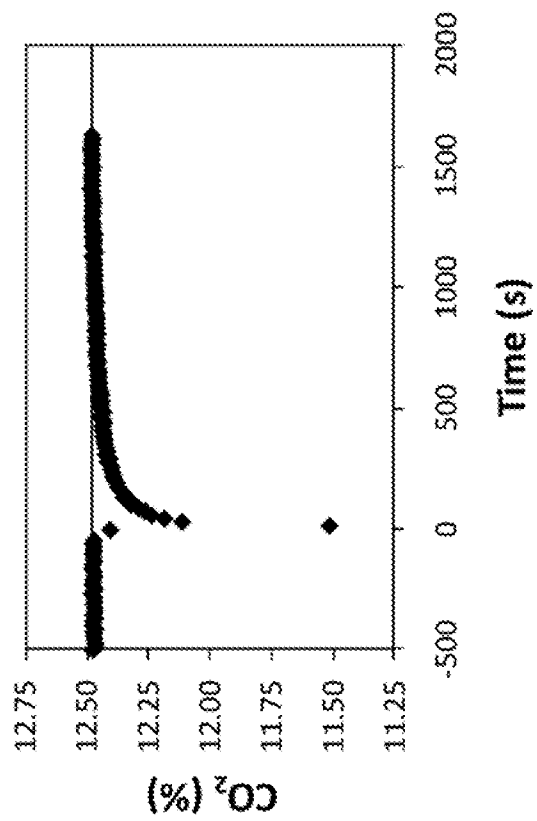


Fig. 5

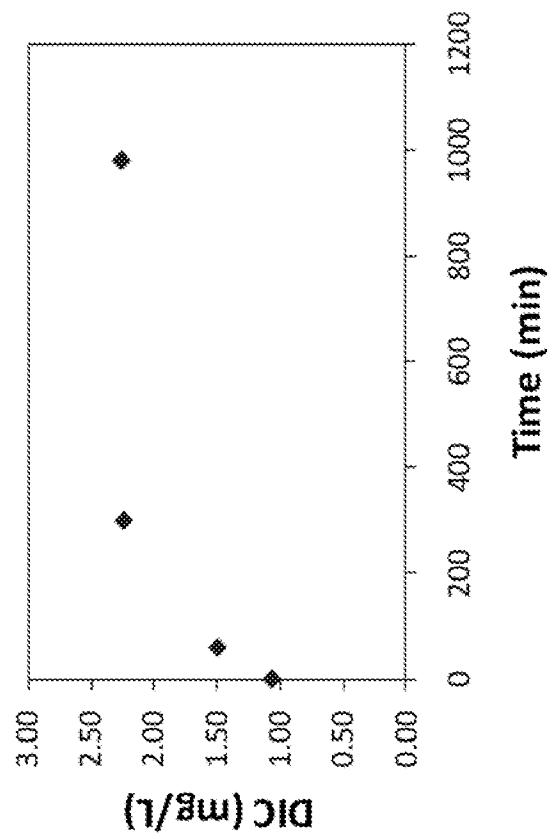


Fig. 6

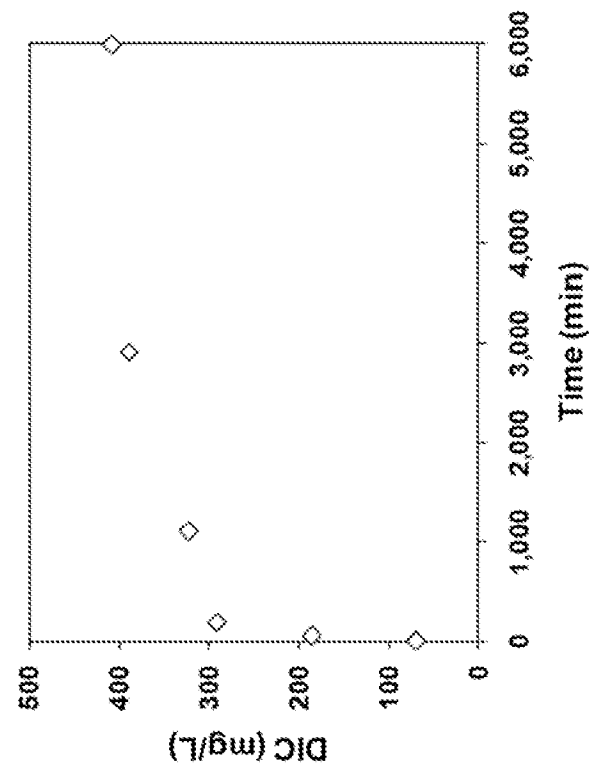


Fig. 7

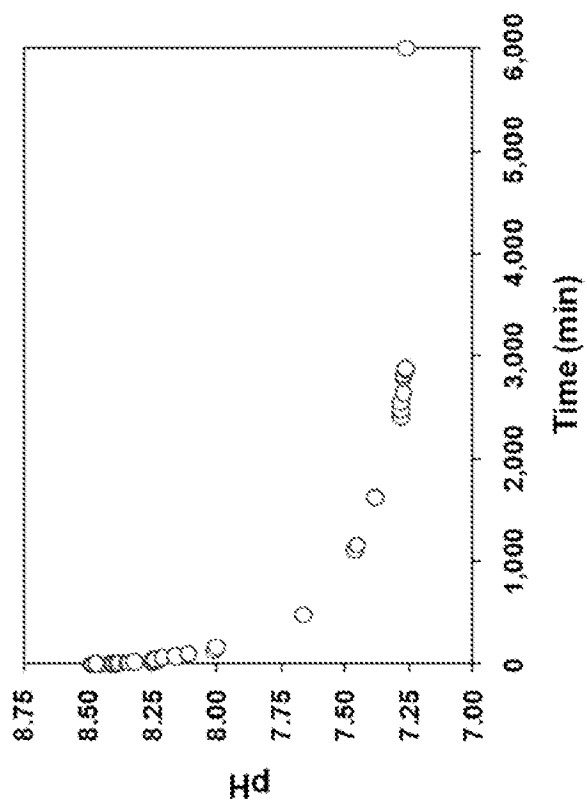


Fig. 8

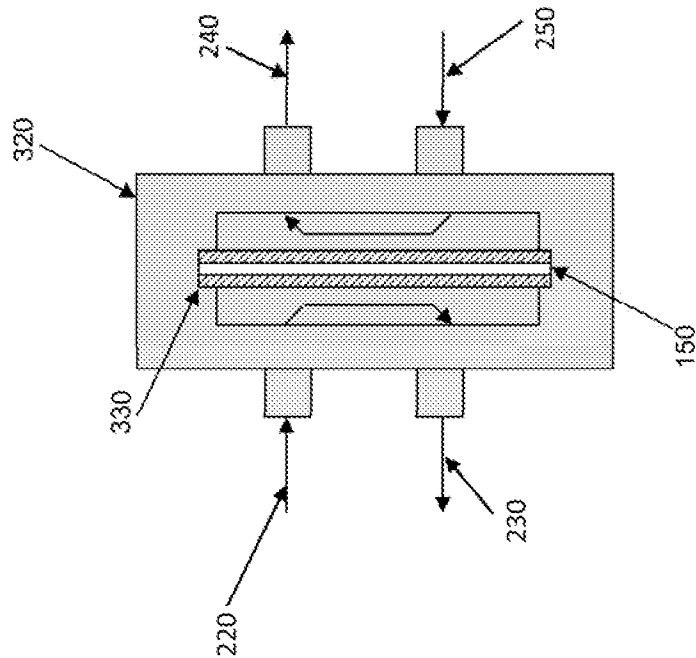


Fig. 9A

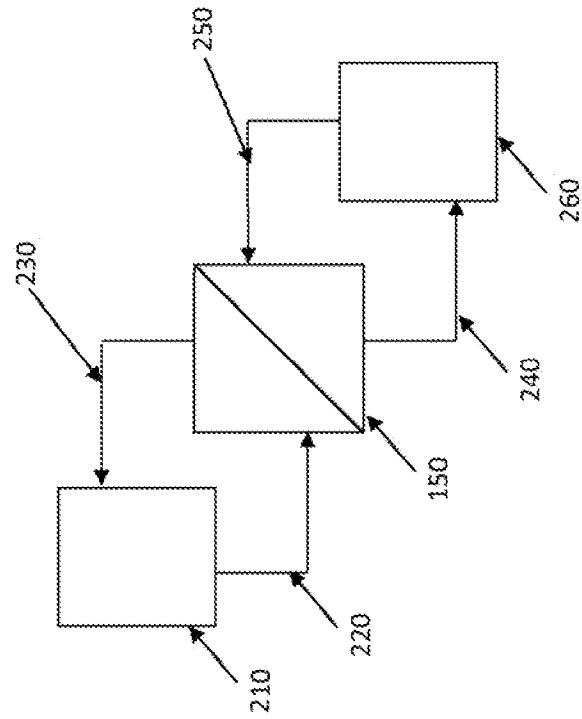


Fig. 9B

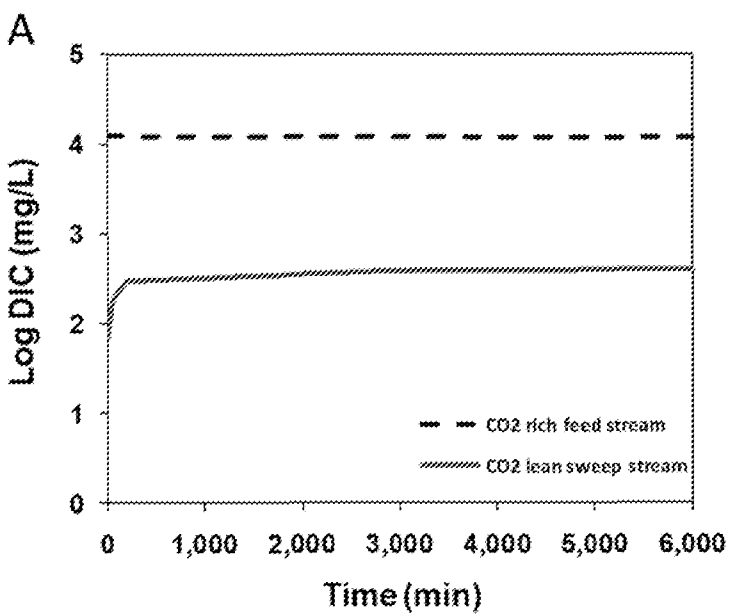


Fig. 10A

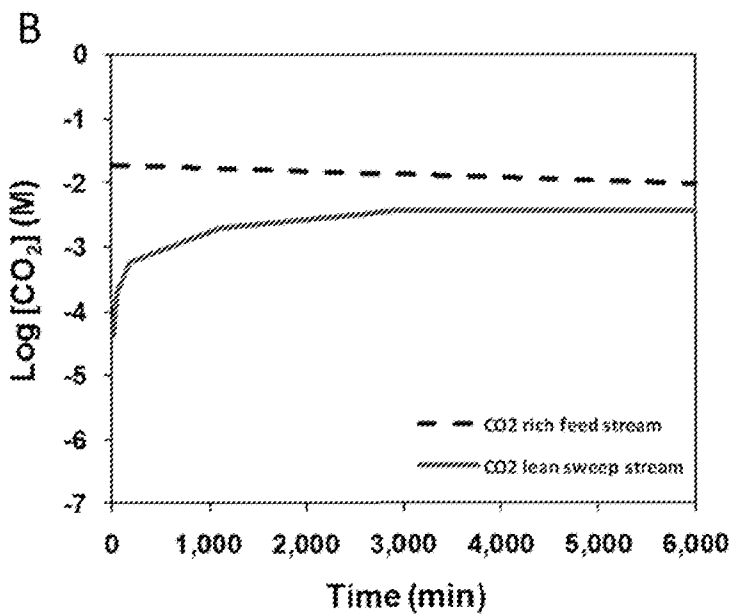


Fig. 10B

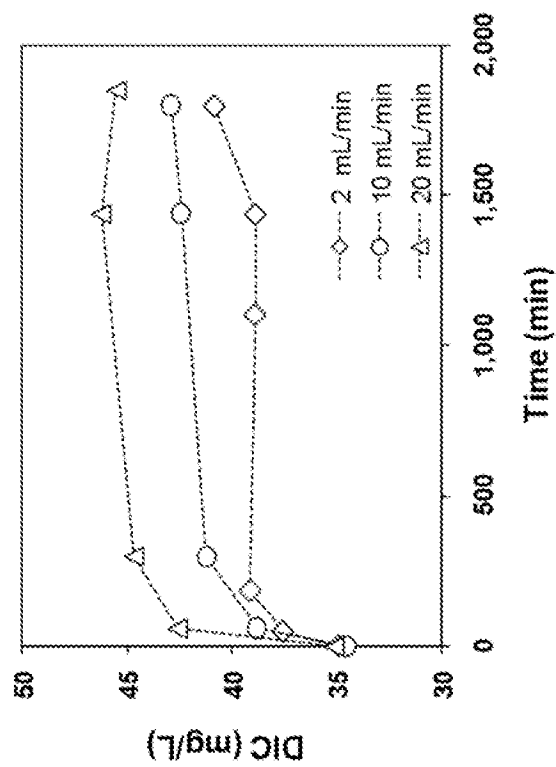


Fig. 11

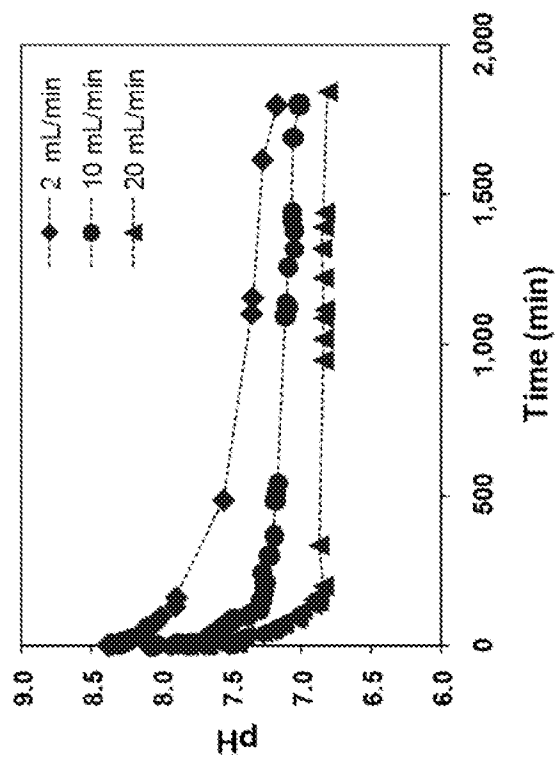


Fig. 12

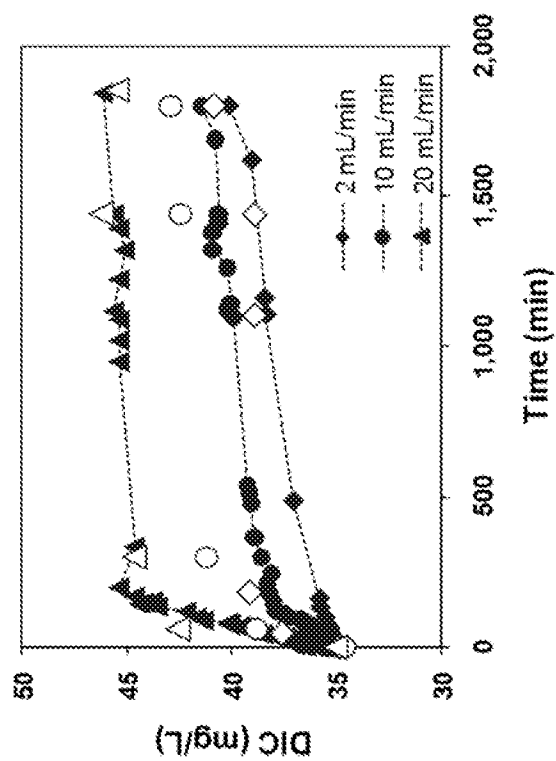


Fig. 13

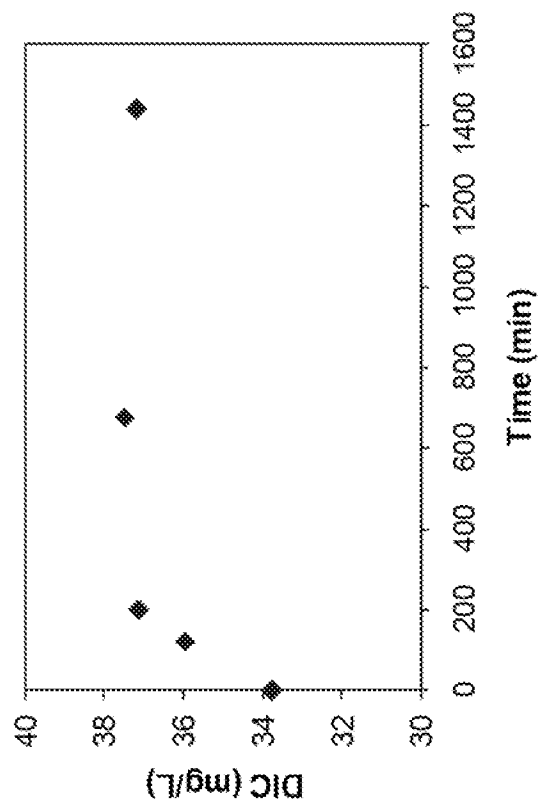


Fig. 14

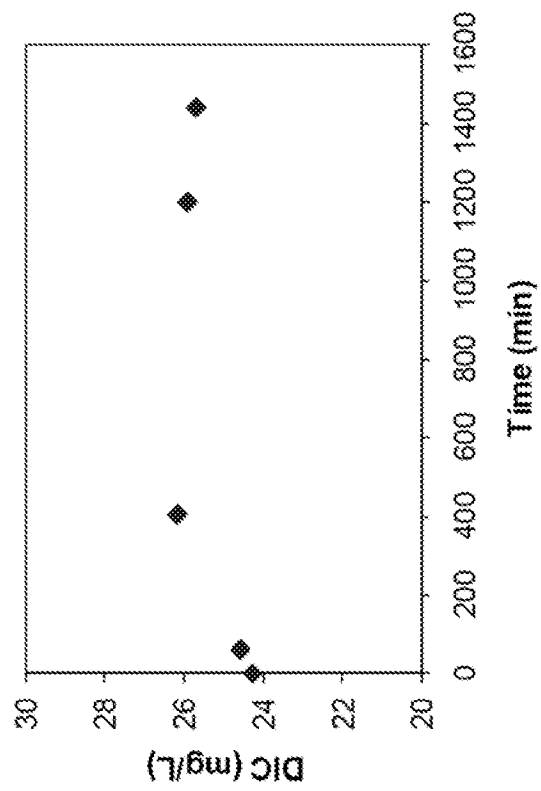


Fig. 15

1

WATER/CARBONATE STRIPPING FOR CO₂ CAPTURE ADSORBER REGENERATION AND CO₂ DELIVERY TO PHOTOAUTOTROPHS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a bypass continuation-in-part of PCT application number PCT/US2010/059684, filed Dec. 9, 2010, which claims priority to U.S. provisional application 61/267,968, filed Dec. 9, 2009. Both applications are incorporated by reference herein in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with government support under Award Number DE-FOA-0000096 awarded by the Department of Energy. The government has certain rights in the invention.

JOINT RESEARCH AGREEMENT

This invention was made as a result of activities undertaken within the scope of a Joint Research Agreement between Algenol Biofuels, Inc. and Georgia Tech Research Corporation.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to the fields of chemistry and biology. More specifically, the invention relates to capture of CO₂ from a gas phase and subsequent delivery of the carbon to a medium promoting the growth of photoautotrophic organisms and the production of biofuels therefrom.

2. Description of the Related Art

Global warming is largely attributed to an increase in atmospheric CO₂, which results from the combustion of fossil fuels. In order to combat this phenomena, a great deal of effort focuses on removal of CO₂ from the atmosphere, industrial sources and gas processing sources via various capture methodologies.

US Patent Application Publication No. 2008/0138265 [leading to U.S. Pat. No. 7,699,909] discloses methods and systems for extracting, capturing, reducing, storing, sequestering, or disposing of carbon dioxide (CO₂), particularly from the air. US Patent Application Publication No. 2008/0087165 to Wright et al. (leading to U.S. Pat. No. 7,708,806 and in the family of PCT Application No. PCT/US2007/080229) discloses the extraction of CO₂ from air using conventional extraction methods or by using a humidity swing or electro dialysis method, and the subsequent delivery of CO₂ to a greenhouse or algal culture using a porous membrane. US Patent Application Publication No. 2009/0232861 to Wright et al. discloses the extraction of CO₂ from a fluid stream and the delivery of CO₂ to controlled environments using a porous membrane, where the CO₂ is utilized by a secondary process. US Patent Application Publication No. 2009/0120288 discloses the removal of carbon dioxide, from ambient air various sorbent technologies. In addition, there are numerous publications and patents describing capture and sourcing of CO₂ from anthropogenic streams (e.g., flue gas from coal fired power plants).

In adsorption-based CO₂ capture, the regeneration of the loaded adsorbent poses several potential hurdles. Of primary concern is the amount of energy required, i.e. steam genera-

2

tion, and chemical stability of the sorbent within the stripping environment, especially for amine-functionalized sorbents in a steam stripping environment. In addition the delivery of CO₂ to algal photobioreactors must also overcome several technical challenges including the need to deliver pure CO₂ to the reactor and minimize the headspace volume that nitrogen and other inert gases occupy in the photobioreactor, the solubility limit of CO₂ in the aqueous phase if delivery through the water stream is preferred, the energy penalties incurred with transport of large volumes of gas to many modular reactors if gas phase delivery is selected and the need to avoid alteration of the ionic content of the photoautotrophic culture medium, which could compromise the health and productivity of the photoautotrophs. None of the cited references addresses these concerns. However, in the present invention we present a process invention for integrated sorbent regeneration and CO₂ delivery that addresses these technical concerns.

BRIEF SUMMARY OF THE INVENTION

The utilization of low energy regeneration of adsorbent (no steam generation needed), simple low energy chemistry, and inexpensive active materials, e.g., soda ash, are utilized to provide for effective CO₂ loading in water or growth media for photoautotroph growth.

An object of this invention is a system for delivering carbon, in the form of CO₂ or bicarbonate, to a photoautotroph for the purpose of increasing the carbon available for consumption by the photoautotrophs, this being accomplished without ionic transport through the membrane to the photoautotrophic culture. In preferred embodiments, the system uses a CO₂ selective dense (non-porous) membrane to minimize or eliminate ionic transport through the membrane while providing a highly selective, facile transfer of CO₂ through the membrane and into the culture medium for consumption by the photoautotrophs.

A further object of this invention is a system for delivering carbon to a photoautotroph wherein resistance to mass transfer through a CO₂ selective membrane is minimized by increasing shear mixing at a surface of the membrane. In some embodiments, shear mixing is increased by increasing the flow rates of fluids across the surfaces of the membrane. In some embodiments, a baffle is disposed on a surface of the membrane or within the membrane housing element to increase shear mixing at the membrane surface.

In a first aspect, the invention provides a system for delivery of carbon to a photoautotroph. The system comprises a stream containing CO₂; a solid adsorbent comprising an amine or other solid sorbent suitable for CO₂ capture; a carbonate-based stripping fluid; a device for washing the CO₂ loaded sorbent with the carbonate stripping solution, thereby allowing the removal of CO₂ from the sorbent and formation of a bicarbonate contacting solution; a CO₂ selective dense (non-porous) membrane incorporated into a module allowing transfer of molecular CO₂ between the bicarbonate rich contacting fluid and a photoautotroph culture medium; and a microfiltration membrane which prevents direct contact between the algae and the bicarbonate contacting solution, wherein the photoautotroph culture medium is enriched with bicarbonate providing carbon for algal growth.

In a second aspect, the invention provides a method for delivering carbon to a photoautotroph. The method comprises providing a stream containing CO₂; passing the CO₂ over a solid adsorbent comprising an amine or other solid sorbent suitable for CO₂ capture; passing a carbonate-based stripping fluid over the CO₂ loaded sorbent, thereby allowing the removal of CO₂ from the sorbent and formation of a bicar-

bonate contacting solution; utilizing a CO₂ selective dense (non-porous) membrane that allows the transfer of molecular CO₂ between the bicarbonate rich contacting fluid and a photoautotroph culture medium; and utilizing a microfiltration membrane to prevent direct contact between the algae and the bicarbonate contacting solution, wherein the photoautotroph culture medium is enriched with bicarbonate providing carbon for algal growth.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects and advantages of this invention will become better understood with regard to the following description, appended claims and accompanying drawings where:

FIG. 1 is a schematic of an integrated system illustrating elements of the first embodiment of the invention.

FIG. 2 is a schematic of a system without the CO₂ selective membrane (Example 2).

FIG. 3 shows a schematic diagram and carbon streams of the overall process in which a first operational mode of the adsorption column (1) is sorption of CO₂ from a flue gas feed stream and a second operational mode (2) is the desorption of CO₂ from the sorbent.

FIG. 4 gives details of an experiment for carbonate stripping.

FIG. 5 gives the gas phase analysis demonstrating CO₂ capture with an APTES sorbent and quantifies the amount of CO₂ on sorbent to be stripped by carbonate solution.

FIG. 6 gives the dissolved inorganic carbon (DIC) concentration of the aqueous solution as a function of time during the packed bed desorption experiment.

FIG. 7 gives the dissolved inorganic carbon (DIC) concentration in the CO₂ lean stream as a function a time which indicates CO₂ flux across the PDMS membrane.

FIG. 8 gives real time pH measurements as a function of time in the CO₂ lean stream as a function a time indicating CO₂ flux across the PDMS membrane.

FIGS. 9A and B illustrate A) a membrane contactor design in which the membrane is supported by two porous metal supports, and B) the experimental set up of a liquid/liquid membrane contactor.

FIGS. 10A and B show A) the dissolved inorganic carbon (DIC) concentration and B) the aqueous CO₂ concentration of each solution as a function of time during the liquid/liquid membrane contactor experiment (Example 3).

FIG. 11 shows dissolved inorganic carbon (DIC) concentration in the receiving solution as a function a time at different flow rates.

FIG. 12 shows real time pH measurements as a function of time in a receiving solution as a function of flow rate.

FIG. 13 shows a comparison of TOC analyzer measured dissolved inorganic carbon (DIC) concentration (open symbols) and pH derived DIC (closed symbols) in a receiving solution at the three flow rates.

FIG. 14 shows concentration of DIC as a function of time in the bicarbonate solution in contact with the APTES sorbent in Example 4, with initial concentration of 33.76 mg/L and final concentration of 37.18 mg/L.

FIG. 15 shows concentration of DIC as a function of time in the synthetic seawater solution in Example 4, with initial concentration of 24.28 mg/L and the final concentration of 25.71 mg/L.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term “photoautotroph” refers to algae and cyanobacteria; more particularly it refers to macro algae or micro algae or cyanobacteria. As used herein, the term “macro algae” (seaweeds) refers to eukaryotic multicellular

plants growing in salt, brackish or fresh water. They are classified into three broad groups based on their pigmentation: i) brown seaweed (Phaeophyceae); ii) red seaweed (Rhodophyceae) and iii) green seaweed (Chlorophyceae). Non-limiting examples include: *Laminaria*, *Undaria*, *Gracilaria*, *Ascophyllum*, *Euchetuna*, *Macrocystis*, *Lessonia*, *Chondrus*, *Sargassum*, and *Hizikia*.

As used herein, the term “micro algae” refers to eukaryotic photoautotrophic organisms that may be unicellular or filamentous and found to be growing in salt, brackish, and fresh water or growing on land (terrestrial species). Non-limiting examples of eukaryotic micro algae include the diatoms (Bacillariophyceae), the green algae (Chlorophyceae), and the golden algae (Chrysophyceae) and all those described in Eukaryotic Microalgae Genomics: The Essence of Being a Plant by Steven G. Ball ((2005) Plant Physiology 137: 397-398).

As used herein, the term “dense (non-porous) membrane” means a membrane with no detectable pores. See Koros et al., “Technology For Membranes And Membrane Processes (IUPAC Recommendations 1996),” Pure and Applied Chemistry, Vol. 68, pp. 1479-1489 (1996).

As used herein, the term “glassy polymer” means an amorphous polymer at temperatures below its glass-transition temperature. See Meille et al., “Definitions Of Terms Relating To Crystalline Polymers (IUPAC Recommendations 2011),” Pure and Applied Chemistry, Vol. 83, pp. 1831-1871 (2011).

As used herein, the term “rubbery polymer” means a macromolecular material such as rubber or a synthetic material having similar properties that returns rapidly to approximately the initial dimensions and shape after substantial deformation by a weak stress and release of the stress. McGraw-Hill Dictionary of Architecture and Construction (2003).

Cyanobacteria are photoautotrophic, prokaryotic organisms that may be unicellular or filamentous. Non-limiting examples include species of *Chamaesiphon*, *Chroococcidiopsis*, *Arthrospira*, *Anabaena*, *Chlorogloeopsis*, *Chroococcus*, *Dermocarpella*, *Geitlerinema*, *Anabaenopsis*, *Fischerella*, *Cyanothece*, *Myxosarcina*, *Leptolyngbya*, *Aphanizomenon*, *Dactylococcopsis*, *Pleurocapsa*, *Lyngbya*, *Calothrix*, *Gloeobacter*, *Stanieria*, *Microcoleus*, *Cylindropspermum*, *Gloeocapsa*, *Xenococcus*, *Oscillatoria*, *Microchaete*, *Gloeotheca*, *Pseudanabaena*, *Nodularia*, *Microcystis*, *Spiulina*, *Nostoc*, *Synechococcus*, *Symploca*, *Scytonema*, *Synechocystis* and *Tolypothrix*.

An important aspect of the present invention is a process concept for integrated sorbent regeneration and CO₂ delivery that addresses technical concerns found in the prior art. This concept is illustrated in FIG. 1 which depicts a system for delivery of carbon species to a photoautotroph comprising a CO₂ feed stream 100, a solid sorbent 110 suitable for CO₂ capture, a carbonate-based stripping solution 120, a device 130 for contacting the CO₂ feed stream 100 with the solid sorbent 110 and washing the CO₂ loaded sorbent 110 with the carbonate stripping solution 120, thereby allowing the removal of CO₂ from the sorbent 110 and formation of a bicarbonate contacting solution 140, a CO₂ selective membrane 150 incorporated into a module allowing transfer of CO₂ between the bicarbonate rich contacting solution 140 and carbon-lean photoautotroph culture medium 160, a microfiltration membrane 170 which prevents direct contact between the photoautotrophs, such as algae, and the bicarbonate contacting solution 140 and a suspension culture 180 of photoautotrophs, from which carbon-lean culture medium 160 is drawn and to which carbon-rich culture medium 190 is returned from the CO₂ selective membrane 150 and photoautotroph-rich broth 200 is returned from the microfiltration membrane 170. The suspension culture 180 may be contained in a vessel such as, for example, a photobioreactor.

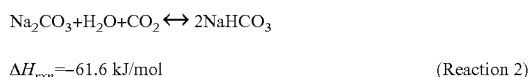
5

Embodiments of the concept illustrated in FIG. 1 could involve one sorbent **110** bed, or more than one sorbent **110** bed. The one sorbent **110** bed embodiment could be accomplished with the one sorbent **110** bed sorbing CO₂ at night, from ambient air for example, and desorbing/stripping during the day as that would match the demand pattern of photoautotrophs.

Reaction 1 illustrates a photosynthetic process whereby a photoautotroph converts CO₂ and water to ethanol, creating a CO₂ driving force across the membrane.



This process concept is based on the chemical reaction of carbonate with CO₂ and water to form a bicarbonate. The reaction of sodium carbonate to form sodium bicarbonate is illustrated in Reaction 2 (computed using Heats of Formation of all species from Felder and Rousseau, Principles of Chemical Processes, 3rd ed., Joint Wiley and Sons, 2005).

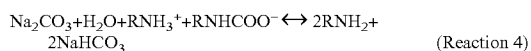


The complete regeneration of an amine-based based sorption system involves removal of CO₂ from the carbamate complex that is formed during capture. The carbamate formation reaction is shown in Reaction 3.

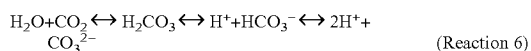


It should be noted that the heat of reaction shown above is that for primary amines reacting with CO₂ (Kim, I, Hoff, K. A., Hessen E. T., Haug-Warberg, T., Svendsen, H. F., Enthalpy of absorption of CO₂ with alkanolamine solutions predicted from reaction equilibrium constants, Chemical Engineering Science, 64(9), 2009, 2027; Kim, I., and Svendsen, H. F., Heat of absorption of carbon dioxide (CO₂) in monoethanolamine (MEA) and 2-(aminoethyl)ethanolamine (AEEA) solutions, Industrial & Engineering Chemistry Research 46 (2007), pp. 5803; and Lee, L. L., 1996. Thermodynamic models for natural gas sweetening fluids. Report on GPI/GPA Project 5091-260-2288. University of Oklahoma, Norman, Okla., USA, pp. 216). A typical solid adsorbent used for CO₂ capture may be comprised of primary, secondary and tertiary amines. As a result the effective heat of reaction is expected to be in the range of -50 to -85 kJ/mol CO₂.

The net heat of reaction for removal of CO₂ from the loaded adsorbent into the aqueous phase is the difference in reaction energies from Reaction 2 minus Reaction 3, thereby producing a low regeneration energy requirement of about 18.4 kJ/mol (Reaction 4).



This approach also utilizes the chemistry of bicarbonate conversion to drive CO₂ into the aqueous phase. The sodium bicarbonate (NaHCO₃) will disassociate and react to form a mixture of aqueous CO₂, H₂CO_{3(aq)}, HCO₃⁻, CO₃²⁻, Na⁺, NaHCO_{3(aq)}, and Na₂CO_{3(aq)} (Reactions 5 and 6) dependent on the ionic strength of solution, total concentration of sodium, total concentration of inorganic carbon, and pH.



The pH and ionic strength of the solution play a crucial role in the total amount of inorganic carbon that can be dissolved into solution. For example at a pH of 8.25 and a partial

6

pressure of CO₂ at 380 ppm (the average pH of sea water under ambient conditions and the concentration of CO₂ in the air), deionized water has 3.1 times less total dissolved inorganic carbon (DIC) capacity than the total DIC capacity of sea water (12.53 mg/L and 38.95 mg/L respectively). Dissolved inorganic carbon is the sum of the inorganic carbon species (CO₂, H₂CO₃, HCO₃⁻, and CO₃²⁻) written in units of mg of carbon per liter. The dominant carbon species differs at different pH values between deionized water and sea water. The dominant aqueous carbon species of deionized water is CO_{2(aq)} at pH<6.35, HCO₃⁻ between at pH>6.35 and pH<10.33, and CO₃²⁻ at pH>10.33, while the dominant aqueous carbon species in sea water is CO_{2(aq)} at pH<5.85, HCO₃⁻ at pH>5.85 and pH<8.92, and CO₃²⁻ at pH>8.92. Carbon concentrations are calculated from solubility products defined by Zeebe and Wolf-Gladrow, CO₂ in Seawater: Equilibrium, Kinetics, Isotopes. Elsevier: Amsterdam; N.Y., 2001; p 251-255. By controlling the pH, ionic strength, sodium and initial carbon concentrations, one can create a solution that can both desorb CO₂ from a solid sorbent to become carbon enriched and be able to create a CO₂ concentration gradient that can be used to deliver CO₂ to a receiving reservoir.

In various embodiments of the invention, the sorbent **110** may be a solid made of porous inorganic, polymer with amine functionality (primary, secondary, tertiary or any combination thereof) including ion exchange resins which form quaternary amine salts, or any other material which has a suitable binding energy for the physisorption or chemisorption of CO₂. For example, see Youssef Belmabkhout and Abdelhamid Sayari, Adsorption (2009) 15: pp. 318-328 for suitable examples yielding low energy requirements in the combination of Reaction 2 minus Reaction 3.

Cyanobacteria have been shown to utilize aqueous CO₂, HCO₃⁻ and CO₃²⁻ as the source of carbon for photosynthesis (to produce biofuels and other products). Dissolved inorganic carbon (DIC) concentration is defined as the total concentrations (grams carbon/liter) of CO₂, HCO₃⁻, and CO₃²⁻. The form of carbon used by the microalgae is not a critical issue because reactions that interconvert CO_{2(aq)}, H₂CO₃, HCO₃⁻ and CO₃²⁻ are sufficiently fast as to not be limiting steps in carbon demand by the photoautotrophs. In the CO₂ selective membrane only molecular CO₂ will pass through the membrane, i.e., there is no ionic transport that can be measured. When the CO₂ transfers to the CO₂ lean stream, it will disassociate quickly to another form of inorganic carbon dictated by the pH of the solution. The difference between aqueous concentrations of CO₂ on both sides of a membrane must be high enough to ensure CO₂ flux across the membrane.

The utilization of this type of chemistry allows for the removal of CO₂ from the loaded sorbent **110** under milder conditions than permitted by other options such as high temperature or steam stripping desorption. This approach also utilizes the chemistry of bicarbonate conversion to drive CO₂ into the aqueous phase. The sodium bicarbonate can be delivered directly to the photobioreactors where the algae can use it as a carbon source. Although cyanobacteria fix carbon as CO₂ by the enzyme RubisCO, most of the carbon that is taken up by the cell can be HCO₃⁻ (See PCT/EP2009/000892). The solubility of sodium bicarbonate in water (about 1M at room temperature) ensures adequate CO₂ delivery to the reactors.

Briefly, a sodium carbonate in water solution **120** (bicarbonate lean) is employed to remove the CO₂ from the loaded sorbent **110**, thereby converting the carbonate to bicarbonate (Reaction 2). Two concepts are proposed. FIG. 1 illustrates the first process concept. Here a closed system is used for the adsorbent stripping. The loaded sorbent **110** bed is contacted with a sodium carbonate stripping solution **120**. The CO₂ is

removed through the formation of bicarbonate in the water phase. This bicarbonate rich solution **140** is then passed over a CO₂ selective dense (non-porous) membrane **150** which is swept with seawater broth (carbonate rich) **160** from the suspension culture **180** in the photobioreactor. Molecular CO₂ moves across the CO₂ selective dense (non-porous) membrane **150** in response to the driving force provided by the chemical potential gradient across the CO₂ selective dense (non-porous) membrane **150** and the bicarbonate rich solution **190** is returned to the suspension culture **180** in the photobioreactor. In order to prevent biofilm formation on the permeation side of the CO₂ selective dense (non-porous) membrane **150**, the solution **160** removed from the suspension culture **180** is first passed through a micro/ultrafiltration membrane **170** to remove the algae.

The device **130** for contacting the CO₂ feed stream **100** with the solid sorbent **110** and washing the CO₂ loaded sorbent **110** with the carbonate stripping solution **120**, thereby allowing the removal of CO₂ from the sorbent **110** and formation of a bicarbonate contacting solution **140**, may be designed and constructed utilizing Perry's Chemical Engineers' Handbook, Eighth Edition, ISBN: 0071422943, Authors: Green, Don W. and Perry, Robert H.

In a first aspect, the invention provides a system for delivery of carbon to a photoautotroph. The system comprises a stream containing CO₂ **100**; a solid sorbent **110** comprising an amine suitable for CO₂ capture; a carbonate-based stripping fluid **120**; a device **130** for washing the CO₂ loaded sorbent **110** with the carbonate stripping solution **120**, thereby allowing the removal of CO₂ from the sorbent **110** and formation of a bicarbonate contacting solution **140**; a CO₂ selective dense (non-porous) membrane **150** incorporated into a module allowing transfer of molecular CO₂ between the bicarbonate rich contacting fluid **140** and a photoautotroph culture medium **160**; and a microfiltration membrane **170** which prevents direct contact between the algae and the bicarbonate contacting solution **140**, wherein the photoautotroph culture medium **190** is enriched with bicarbonate providing carbon for algal growth.

In a second aspect, the invention provides a method for delivering carbon to a photoautotroph without altering the ionic content of the culture medium. The method comprises providing a stream **100** containing CO₂; passing the CO₂ over a solid sorbent **110** comprising an amine suitable for CO₂ capture; passing a carbonate-based stripping fluid **120** over the CO₂ loaded sorbent **110**, thereby allowing the removal of CO₂ from the sorbent **110** and formation of a bicarbonate contacting solution **140**; utilizing a CO₂ selective dense (non-porous) membrane **150** that allows the transfer of molecular CO₂ between the bicarbonate rich contacting fluid **140** and a photoautotroph culture medium **160**; and utilizing a microfiltration membrane **170** to prevent direct contact between the algae and the bicarbonate contacting solution **140**, wherein the photoautotroph culture medium **190** is enriched with bicarbonate providing carbon for photoautotroph growth.

The second concept uses an open system where the CO₂ depleted culture Medium **160** is used as the CO₂ stripping medium. Here the culture medium **160** is passed through a microfiltration membrane **170**, and then fed into the CO₂ saturated sorbent **110**. This concept is advantageous where volatile products, such as ethanol, have been removed from the reac culture medium **160** as part of the CO₂ collection strategy.

The invention described herein may be utilized to provide CO₂ to open ponds or closed photobioreactors.

EXAMPLES

The following examples illustrate embodiments of the invention. Example 1 presents options for the CO₂ source

100, the sorbent **110** for CO₂, the configuration of the contactor/stripping device **130**, the composition of the carbonate stripping fluid **120**, the CO₂ selective dense (non-porous) membrane **150**, and the microfiltration membrane **170**. Example 2 presents an embodiment wherein the stripping fluid **120** comprises a filtered bicarbonate lean stream **160** from the suspension culture **180** in the photobioreactor or photobioreactors. Example 3 presents working embodiments of CO₂ adsorption and desorption and CO₂ delivery in support of the invention. Example 4 presents a working embodiment of integrated CO₂ adsorption and desorption and CO₂ delivery in support of the invention. Example 5 presents a prophetic example of economic modeling.

A total carbon (TC) analyzer (Shimadzu TOC-VCPH) was used to determine dissolved inorganic carbon concentrations in aqueous solutions. An inorganic carbon calibration was performed daily before each measurement using carbon standard solutions. A quadrupole mass spectrometer (Pfeiffer Vacuum OminStar™ Gas Analysis System) was used to determine the gas concentrations during the carbon dioxide sorption studies. A Mettler Toledo pH meter was used to measure the pH of the aqueous solutions in real time, while peristaltic pumps were used to circulate the aqueous solutions.

All chemicals used in experiments were ACS grade or better. Water used in the experiments was deionized (>15 MΩ·cm) using a Millipore Elix. Sylgard® 184 Silicone Elastomer Base and Curing Agent were used to synthesize the polydimethylsiloxane (PDMS) membranes. The 3-aminopropyltriethoxysilane (APTES) functionalized glass beads (30-50 μm) were purchased from Polyscience, Inc. (Cat#23584) and used as the CO₂ sorbent. Synthetic sea water was made by mixing Instant Ocean® salts with deionized water to simulate photobioreactor broths.

Example 1

Regeneration of a CO₂ Loaded Adsorber with Carbonate Solution Using a CO₂-Selective Dense (Non-Porous) Membrane System

The source **100** of CO₂ may be air, flue gas from power plants or industrial sources, or natural gas treating.

The sorbent **110** may be a solid made of: porous inorganic, polymer with amine functionality (primary, secondary, tertiary or any combination) including ion exchange resins which form quaternary amine salts, or any other material which has a suitable binding energy for the physisorption or chemisorption of CO₂. These are well known in the art.

The contactor/stripping device **130** configuration may be a packed bed with low pressure drop sorbent **110** particles which may be mixed with inorganic components to increase porosity and limit pressure drop, a honeycomb monolithic ceramic supporting a suitable CO₂ adsorbent, or an inorganic-organic hybrid or polymer based fiber contactor made of functionalized amine, amine rich polymer or polymer loaded with ion exchange resin. These are well known in the art. CO₂ sorbent systems that are consistent with the extraction of CO₂ via carbonate contacting fluid may be selected to design the sorbent module in a manner which optimizes the stripping process described below.

The stripping solution **120** may be an aqueous carbonate preferentially sodium, but also potassium. The concentration of the stripping solution **120** may range from 0.01 to 0.55M (1 mole goes to 2 moles of bicarbonate which has solubility limit of 1.19M in water). The stripping solution **120** may also contain other salts and metals such as found in seawater.

The contactor/stripping device **130** is designed to allow the loaded sorbent **110** to be washed with stripping solution **120**. The contactor/stripping device **130** will also allow for the heating of the stripping solution **120** in the range of 10 to 50 degrees Celsius above ambient temperature. The contactor/stripping device **130** will include a means for delivery of the stripping solution **120** such that the solution may have a residence time in the contactor/stripping device **130** from 30 seconds to 30 minutes. The stripping solution **120** will be converted from carbonate rich to bicarbonate rich and leave the regenerated sorbent **110** as a contacting solution **140** with a bicarbonate concentration from 0.02 to 1.1 M with the balance of the carbonate from the lean solution **120** being un-reacted carbonate.

In an embodiment wherein photoautotrophs are present in a suspension culture **180** in a photobioreactor or photobioreactors, the CO₂ selective dense (non-porous) membrane **150** takes a flow of the bicarbonate rich solution **140** on one side (retentate) and is swept with filtered culture fluid **160** (carbonate rich) from the photobioreactors on the other side (permeate). Such a system is not known in the art. The carbonate chemistry in water allows photoautotrophs to deplete the CO₂ concentration through the consumption of CO₂ and HCO₃⁻. The driving force for CO₂ transport across the CO₂ selective dense (non-porous) membrane **150** is the chemical potential gradient moving toward the carbonate/bicarbonate equilibrium of the two fluids that is caused by the consumption of CO₂ by the photoautotrophs to form ethanol, biomass or other products. The CO₂ selective dense (non-porous) membrane **150** may be composed of a non-porous rubbery polymer such as polydimethylsiloxane or a glassy polymer chosen from a number of families with operating pore sizes smaller than the size of a hydrated sodium cation or a hydrated carbonate or bicarbonate anion, such as cellulose acetate, polyimides or polyether sulfones, or the membrane may be of layered construction containing polymers of any or all of the classes mentioned above. The CO₂ permeability of the CO₂ selective dense (non-porous) membrane **150** may be in the range of 100-10,000 Barrer. In some embodiments, the CO₂ selective dense (non-porous) membrane **150** is polydimethylsiloxane (PDMS) with a CO₂ permeability of 3800 Barrer (1.27×10^{-12} mol/m-s-Pa) at 35° C. In this device, CO₂ moves across the CO₂ selective dense (non-porous) membrane **150** converting the bicarbonate lean solution **160** from the photobioreactor to a bicarbonate rich solution **190**, which is then returned to the bioreactor.

The microfiltration membrane **170** filters the photoautotrophs from the culture in order to prevent biofilm formation on the permeation side of the CO₂ selective dense (non-porous) membrane **150** (due to the high concentration of bioavailable CO₂). The culture medium **160** removed from the reactor is first passed through a micro/ultrafiltration membrane **170** to remove the photoautotrophs. The micro/ultrafiltration membrane **170** must have an effective pore size in the range of 0.05-5 µm and may be chosen from any number of commercially available microfiltration membranes made from ceramic or polymeric materials, which are all well known in the art.

Example 2

Regeneration of CO₂ Loaded Adsorber Using a Stripping Solution Comprising a Bicarbonate Lean Broth from Reactor as Stripping Solution

As illustrated in FIG. 2, this example uses the same elements of Example 1 but comprises a filtered bicarbonate lean stream **160** from the photobioreactors as the stripping solu-

tion **120**. The same concentration ranges apply and same microfiltration membrane **170** would be used.

Example 3

Demonstration of a CO₂ Desorption from a CO₂ Loaded Sorbent Using a Carbonate Solution and CO₂ Transfer Between Aqueous Solutions Using a CO₂ Selective Dense (Non Porous) Polymer Membrane

In the CO₂ adsorption column illustrated in FIG. 3, CO₂ from the feed stream **100**, in this case a CO₂ rich flue gas, is adsorbed by the sorbent **110** and exits as a CO₂ stripped flue gas **102**. The CO₂ is desorbed from the solid sorbent **110** by a water carbonate stream **120** in which the sodium carbonate (Na₂CO₃) reacts with the surface and removes complexed CO₂ held as RNHCOO⁻ to form sodium bicarbonate consistent with Reaction 2. The sodium bicarbonate reacts to a dissolved inorganic form and becomes enriched in dissolved inorganic carbon. The contacting solution **140** is delivered to a water carbonate reservoir **210**. After some time an enriched carbon stream **220** is pumped in contact with the CO₂ selective dense (non-porous) membrane **150** into which aqueous CO₂ dissolves. The membrane retentate **230** has less CO₂ corresponding to a lower DIC concentration than the enriched carbon stream **220**. The membrane permeate **240** is enriched in CO₂ corresponding to a higher DIC concentration than a feed stream **250** from a receiving solution reservoir **260**. After some time, the receiving solution reservoir **260** reaches a DIC concentration usable by microorganisms in the photobioreactor (PBR). The PBR feed **190** contains carbon that is consumed to make ethanol or other biofuels. A biofuel stream **270** is removed from the PBR and processed further. The PBR algal broth **180** is then pumped through a filter (a micro- or ultrafiltration membrane **170**) in which a return stream **200** is enriched in biosolids and returned back to the suspension culture **180** while a biosolids free stream **160** is returned to the receiving solution reservoir **260** to be enriched in carbon via contact with the CO₂ selective dense (non-porous) membrane **150**. Key aspects of this example are the transfer of molecular CO₂ across the CO₂ selective dense (non-porous) membrane **150** from the water carbonate solution reservoir **210** to the receiving solution reservoir **260**, the lack of any ionic transport across the CO₂ selective dense (non-porous) membrane **150** and the regeneration of the solid CO₂ sorbent **110** using viable stripping solutions **120**.

Sorbing CO₂ onto Absorbent

A packed bed column with a 3-Aminopropyltriethoxysilane (APTES) sorbent **110** was used to remove CO₂ from a CO₂/N₂ gaseous stream **100**. The loaded sorbent **110** was then stripped with an aqueous solution **120** to assess the viability of desorbing CO₂ from the sorbent **110** using an aqueous solution **120**. A conceptual diagram of the setup is illustrated in FIG. 4. A 7 mL column was first filled with 1.31 g of 3 mm of glass beads **280**. Then 1 g of the amine grafted glass bead sorbent **110** purchased from Polyscience, Inc. was placed into the column, then additional 1.73 g of 3 mm glass beads **280** was packed on top of the sorbent **110**. Column frits (10 µm filters) at the top and bottom of the column prevent the movement of glass beads **280** and sorbent **110**. No CO₂ sorption was shown to occur onto the 3 mm glass beads **280**. A 12.5% mol/mol CO₂ (the rest N₂) stream **100** was fed into the column at a rate of 0.05 SCFH (22.39 mL/min).

The amount of CO₂ in the exit stream **102** was measured as a function of a time and the amount of CO₂ adsorbed was calculated using a breakthrough curve (FIG. 5). The adsorption of CO₂ to the amine occurred within ten minutes. The average sorption capacity of the sorbent **110** was determined

11

to be 1.024 mg CO₂ as C/g of sorbent based on single adsorption/regeneration cycles. The working adsorption capacity therefore would be less than 1.0 mg CO₂ as C/g sorbent **110**.

Valves **300** were then changed to allow an aqueous solution **120** to pass over the sorbent **110** to desorb the sorbed CO₂. The aqueous solution **120** was prepared in a Tedlar® bag by weighing out 0.115 g NaOH and pumping in 115 mL of deionized water to eliminate CO₂ transfer to the solution **120** similar to the preparation in the liquid/liquid membrane experiment. The solution **120** was well mixed using a stir bar in the Tedlar® bag and 15 mL of solution was used to determine the initial pH and DIC concentrations giving a final water reservoir volume of 100 mL. The initial pH of the solution **120** was 12.51 and the initial dissolved inorganic carbon (DIC) concentration was 1.073 mg/L. The initial DIC concentration in solution was attributed to CO₂ transfer from the air to the water before the water was pumped into the Tedlar® bags. The aqueous solution **120** was pumped from the bottom of the column to top at a rate of 2 mL/min and returned back to the water reservoir **310**. The change in DIC concentration of the aqueous solution **120** increased as a function of time (FIG. 6) with a final DIC concentration of 2.26 mg/L. The amount of CO₂ desorbed from the sorbent was 0.126 mg as C which corresponds to 80.8% of the total sorbed CO₂.

Desorbing CO₂ into Stripping Solution

The effect of pH on the effective equilibrium of the elutriation of CO₂ was examined. A mass balance on the amount of carbon uptake in the solution **120** was used to calculate the total amount desorbed from the APTES sorbent **110** (Table 1). The results indicated that at higher pH values more CO₂ can be desorbed from the APTES sorbent **110**. However, at higher pH values the stripping solution **120** has less of a CO₂ driving force to promote the transfer of CO₂ across the CO₂ selective dense (non-porous) membrane **150**.

TABLE 1

The percentage of carbon dioxide desorbed from the sorbent 110 under different initial conditions.		
pH	DIC (mg/L)	
	1.0	35
7	19.4%	20.9%
8.25		52.1%
Seawater 8.25		57.4%
10	55.3%	50.9%
12	80.8%	59.4%

The initial concentration of the bicarbonate solution **140** was 12.067 mg as C/L (=12.067 DIC/liter) and the aqueous CO₂ concentration was 1.91×10^{-2} M with an initial pH was 8.06. The initial concentration of CO₂ poor solution **120** was 70.0 mg as C/L and the aqueous CO₂ concentration was 4.14×10^{-5} M with an initial pH of 8.38. Since the aqueous CO₂ concentration was greater in the bicarbonate solution **140**, there was a driving force for CO₂ flux across the CO₂ selective dense (non-porous) membrane **150**. The DIC concentration in the CO₂ poor solution **120** increased with time (FIG. 7) indicating CO₂ flux across the CO₂ selective dense (non-porous) membrane **150**. The pH of the CO₂ poor solution **120** decreased with time (FIG. 8). The pH change was due to the acidification of the solution **120** with the addition of CO₂ and was used as an indirect indicator of CO₂ transfer in systems. The initial flux of CO₂ across the CO₂ selective

12

dense (non-porous) membrane **150** was 3.55×10^{-6} kg/s m² and the total amount of CO₂ transferred in this process was 135.4 mg as C.

CO₂ Transfer Between Aqueous Solutions Using a CO₂ Selective Dense (Non-Porous) Polymer Membrane

A liquid/membrane/liquid contactor experiment was used to determine the viability of using a CO₂ selective dense (non-porous) polydimethylsiloxane (PDMS) membrane **150** to transfer aqueous CO₂ from a bicarbonate (CO₂ rich) aqueous solution **140** to a CO₂ poor receiving solution **160**. The PDMS membrane **150** was supported inside the membrane contactor **320** by two highly porous (2 mm pores) metal supports **330** (0.7 mm thick) (FIG. 9A). A conceptual diagram of the setup is illustrated in FIG. 9B.

The PDMS membrane **150** (92 µm thick) was synthesized by first weighing out 9:1 wt/wt ratio of silicone elastomer base to curing agent and dissolving in heptane to make a 20% wt/wt solution of PDMS in heptane. The solution of 20% wt/wt PDMS in heptane was then pipetted onto a Teflon® plate and placed in a vacuum oven at 80° C. for two hours. After boiling off the heptane, the PDMS film was left to cool at room temperature before removing the film **150** and placed into a permeation cell to determine gas permeability and selectivity. The permeability [Barrer= 10^{-10} cm³(STP)-cm/cm²-s-cmHg)] of the PDMS film **150** was measured with pure gases at 22° C. (CO₂=2170, O₂=398, N₂=206 Barrer). The gas selectivities were then calculated from the permeabilities ($\alpha_{O_2/N_2}=1.9$, $\alpha_{CO_2/O_2}=5.5$, $\alpha_{CO_2/N_2}=10.5$), and confirmed the formation of a PDMS membrane **150**.

The upstream bicarbonate aqueous solution **220** was a 1M NaHCO₃ solution pumped into contact with the membrane contactor **320**. The downstream CO₂ poor solution **250** contained a low dissolved inorganic carbon (DIC) concentration of approximately 35 mg/L DIC, simulating the amount of dissolved inorganic carbon (DIC) found in a photobioreactor solution. A pH probe was placed in the CO₂ poor solution **250** to monitor the change in pH caused by the uptake of CO₂ into solution **250**. At periodic intervals the bicarbonate aqueous solution **220** and the downstream CO₂ poor solution **250** were sampled through the septum valves using a syringe to determine the dissolved inorganic carbon (DIC) concentration using a total organic carbon (TC) analyzer (Shimadzu TOC-VCPH). Sodium concentration was measured with a sodium ion probe in each grab sample. No sodium was observed to transfer across the PDMS membrane **150**, confirming that the PDMS membrane was a dense (non-porous) membrane.

The containers for the bicarbonate aqueous solution **220** and the downstream CO₂ poor solution **250** were 1 L Tedlar® bags with two polypropylene 2-in-1 valves with a septum valve and a 1/8" fitting. The Tedlar® bags were used to eliminate CO₂ transfer between the atmosphere and the solution. The bicarbonate aqueous solution **220** and the downstream CO₂ poor solution **250** were made by weighing out the appropriate amount of sodium bicarbonate, NaHCO₃, (Solution 1=33.604 g and Solution 2=0.1960 g) then with the Tedlar® bag closed air was removed from each bag using the septum valves. Finally, 500 mL of deionized water were pumped into each Tedlar® bag to minimize the amount of gas in each bag. Each aqueous solution was well mixed using stir bars in each Tedlar® bag. Afterwards 100 mL of the solution **220** and **250** were pumped out of each bag and used for initial measurements, leaving a final volume of 400 mL in each bag.

During the experiment the bicarbonate aqueous solution **220** and the downstream CO₂ poor solution **250** were pumped at a flow rate of 2, 10 or 20 mL/min to investigate the effect of flow rate and examine the impact of external mass transfer resistances within the membrane contactor **320**. The flows of

13

the bicarbonate aqueous solution **220** and the downstream CO₂ poor solution **250** were countercurrent and the flowrates were equal in magnitude.

Even though the difference between DIC concentrations of the bicarbonate aqueous solution **220** and the downstream CO₂ poor solution **250** remained large throughout the experiment (FIG. 10A), the DIC concentration in the CO₂ lean solution **250** reached a steady state concentration. The difference between the aqueous CO₂ concentration of the bicarbonate aqueous solution **220** and the downstream CO₂ poor solution **250** became small (FIG. 10B) minimizing the concentration driving force between the two solutions. It is important to consider the difference in aqueous CO₂ concentrations when optimizing this process to other systems which allows the system to be flexible and may not require such a carbonate loaded stream in other processes. For example, to maintain the initial CO₂ flux in the experiment stated above, a DIC concentration of 12,000 mg/L was needed at pH of 8.0 but lower DIC concentrations would be needed at lower pH values (1430 mg/L and 273 mg/L of DIC at pH values 7.0 and 5.0 respectively). Operational pH values of the bicarbonate aqueous solution **220** will be dependent on the sorbent **110** type. The desired pH value could be as low as the sorbent **110** can maintain its structural integrity but will lie within the pH range of 5.0 to 8.2. Bicarbonate aqueous solution **220** with a pH greater than 8.2 with the desired CO₂ flux will have problems with the precipitating out of solids. The operational DIC concentrations of the CO₂ lean stream **250** can vary from 0.31 mg/L (0.03 mM) to 3000 mg/L (250 mM) while the operational pH values of the CO₂ lean stream **250** could vary from 7.0 to 9.0. A high CO₂ flux across the membrane **150** is desired to minimize membrane area and to meet CO₂ delivery demand. In general to achieve a high CO₂ flux, a high pH (>8.0) and a low DIC (<70 mg/L) would be desired on the CO₂ lean stream **250** while a low pH (<7.5) and a high DIC would be desired on the bicarbonate aqueous solution **220**. The monitoring of aqueous CO₂ concentration in each stream is desired to ensure that the concentration in the bicarbonate aqueous solution **220** is greater than the CO₂ lean stream **250** at all times, and can be accomplished by imbedded pH probes to provide real time pH readings, syringe pumps with a desired base (e.g. sodium hydroxide) or a desired acid (e.g. hydrochloric acid), and a direct measure of DIC using a TOC analyzer, infrared spectrometer, or Raman spectrometer.

The initial DIC concentration of each of the CO₂ poor solutions **250** were essentially the same—34.9, 34.6, and 35.1 mg/L—for the flow rates of 2, 10, 20 mL/min, respectively (FIG. 11). The final DIC concentration for each flow rate condition of the CO₂ poor solutions **250** was 40.8, 42.9, and 45.5 mg/L for 2, 10, and 20 mL/min respectively after 30 hours of operation. The pH decreased in the CO₂ poor solution **250** due to the uptake of CO₂ (FIG. 12).

The DIC and pH for all three flow rates would eventually approach the same value. The difference observed at the 2,000 minute mark was due to the time response which was a function of the flow rate and the mass transfer resistances in the membrane contactor **320**. (Experiments run to 80 hours, not shown, revealed a close approach of the DIC and pH values for a 2 mL/min flow rate to those for a 20 mL/min flow rate).

The observed change in pH in the CO₂ poor solution **250** decreased to an approximate value of 0.002 pH units per hour and steadily decreased due to the decrease in the driving force. The increase in DIC concentration in the CO₂ poor solution **250** as indicated by the change in pH correlated with the grab samples measured by the TC analyzer (39.6, 41.4,

14

and 46.1 mg/L for 2, 10, and 20 mL/min respectively). A comparison of the two measures is shown in FIG. 13.

The lingering differences in DIC concentrations at long times indicated significant external mass transfer resistances in the membrane contactor **320**. In the absence of external mass transfer resistance, all three curves in FIG. 13 would superimpose at all time scales, the changes with time reflecting the decrease in driving force across the membrane **150** in “batch” experiments. External mass transfer resistance is reduced by, for example, increasing flow rates of the fluid streams **220** and **250** across the surfaces of the CO₂ selective dense (non-porous) membrane **150** and/or incorporating baffles on the surfaces of the membrane **150**.

In each case studied, the DIC concentration in the CO₂ poor solution **250** rapidly increased but leveled off approaching an asymptotic value. The rate of change continually decreased due to the decrease in driving force. This indicated that even though there still was a significant difference in the amount of DIC in each reservoir (≈1 to 3.5×10⁻³ M in the upstream and downstream reservoirs respectively) the CO₂ driving force across the membrane **150** decreased substantially over time.

The change in the CO₂ chemical potential on both sides of the membrane contactor **320** was investigated. The effective concentrations or activities (α_i) of dissolved species are defined as:

$$\alpha_i = \gamma_i m_i / m^\circ \quad (\text{Equation 1})$$

where γ_i is the activity coefficient and m_i is the molal concentration of species i. The standard state of molality (m[°]) is 1 mol/kg so that Equation 1 can be rewritten as α_i = γ_i m_i. The chemical potential (μ_i) of individual dissolved species is:

$$\mu_i = \mu_i^\circ + RT \ln \alpha_i \quad (\text{Equation 2})$$

where μ_i[°] is the chemical potential of the species at a reference condition. The ionic strength (I) of the solution is defined as:

$$I = \frac{1}{2} \sum (m_i z_i^2) \quad (\text{Equation 3})$$

where z_i is the charge of species i. The activity coefficient (γ_i) is a strongly dependent on ionic strength (I), which is dependent on the concentration of anions and cations. Other factors that affect the activity coefficient include temperature, density of water, dielectric constant of water, and effective size of hydrated ions. The Debye-Huckel equation (Reaction 10) was used to solve for the activity coefficients of charged dissolved aquatic species.

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} \quad (\text{Equation 4})$$

where A = 1.824928 × 10⁶ ρ_o^{1/2} (εT)^{-3/2} and B = 50.3 (εT)^{-1/2}, ρ_o is the density of water, ε is the dielectric constant of water, z_i is temperature in Kelvin, is the ionic charge of species i, and a_i is the ion size parameter of species i. Activity coefficients for uncharged, molecular species obey the empirical Setchenow equation up to high ionic strengths and generally include dissolved gases, weak acids, and molecular organic species. The Setchenow equation (Equation 5) is:

$$\log \gamma_i = K_i I \quad (\text{Equation 5})$$

A 20 mL/min the CO₂ poor solution **250** initially had an ionic strength of 2.94 × 10⁻³ mol/kg yielding an activity coef-

15

ficient of CO₂ ($\gamma_{CO_2,D}$) of 0.9984 and a molar concentration of CO₂ equal to 3.12×10^{-5} M and a CO₂ activity ($\alpha_{CO_2,D}$) of 3.115×10^{-5} . For the CO₂ poor solution **250** at the final sample point (DIC=46 mg/L), the ionic strength was 2.917×10^{-3} mol/kg yielding an activity coefficient of CO₂ ($\gamma_{CO_2,D}$) of 0.9984 and a molar concentration of CO₂ equal to 9.11×10^{-4} M or a CO₂ activity ($\alpha_{CO_2,D}$) of 9.095×10^{-4} .

Similarly, for the bicarbonate aqueous solution **220** the initial (t=0) ionic strength was 0.707 mol/kg, the $\gamma_{CO_2,U}$ =0.6866, $\alpha_{CO_2,D}$ = 1.69×10^{-2} and initial CO₂ concentration= 2.46×10^{-2} M. For the bicarbonate aqueous solution **220** for the final data point the following were calculated for a CO₂ concentration of 2.41×10^{-2} M, $\gamma_{CO_2,U}$ =0.6861 and the $\alpha_{CO_2,D}$ = 1.47×10^{-2} . From the calculated CO₂ activities, the chemical potential of CO₂ in both the bicarbonate aqueous solution **220** and CO₂ poor solution **250** are described as:

$$\mu_{CO_2}^U = \mu_{CO_2}^o + RT \ln \alpha_{CO_2,U} \quad (\text{Equation 6})$$

$$\mu_{CO_2}^D = \mu_{CO_2}^o + RT \ln \alpha_{CO_2,D} \quad (\text{Equation 7})$$

The difference between the bicarbonate aqueous solution **220** and CO₂ poor solution **250** chemical potentials is:

$$\Delta \mu_{CO_2} = \mu_{CO_2}^U - \mu_{CO_2}^D = \mu_{CO_2}^o + RT \ln \alpha_{CO_2,U} - \mu_{CO_2}^o - RT \ln \alpha_{CO_2,D} \quad (\text{Equation 8})$$

$$\Delta \mu_{CO_2} = RT \ln \frac{\alpha_{CO_2,U}}{\alpha_{CO_2,D}} \quad (\text{Equation 9})$$

Equation 9 describes the driving force at initial conditions assuming a perfectly mixed solution. Initially the ratio of the bicarbonate aqueous solution **220** to CO₂ poor solution **250** activity was

$$\frac{\alpha_{CO_2,U}}{\alpha_{CO_2,D}} = 540$$

while after 24 hours the ratio of the bicarbonate aqueous solution **220** to CO₂ poor solution **250** activity decreased to

$$\frac{\alpha_{CO_2,U}}{\alpha_{CO_2,D}} = 16.$$

As can be seen the initial activity of CO₂ in the bicarbonate aqueous solution **220** was 540 times greater than the activity of CO₂ in the CO₂ poor solution **250**. As the experiment progressed the initial activity of CO₂ in the bicarbonate aqueous solution **220** decreased to be 16 times greater than the activity of CO₂ in the CO₂ poor solution **250**. This was a 97% decrease in driving force which explained, to a large degree, the decrease in CO₂ flux across the membrane **150** and indicated that only CO₂ crossed the membrane, which was confirmed by the absence of sodium ion transport during the experiment.

An important design parameter, relevant to potential for process scale up and commercial deployment, is the CO₂ permeance of the membrane **150**. In the case of the fastest flow rate (20 mL/min) there was a change in DIC concentration of 0.25 mg/L within the first 15 seconds, which resulted in an initial CO₂ flux of 0.134 mmol/m²sec and a permeance of about 5 GPU [GPU= 10^{-6} cm³ (STP)/(cm²-s-cmHg)]. In comparison to the expected permeance of 24 GPU determined from gas transport measurements on the same PDMS

16

films, i.e., without liquid mass transfer resistances, the impact of the external mass transfer resistance was about a factor of five reduction in CO₂ flux. The magnitude of this effect is consistent with the observations illustrated in FIGS. **11**, **12** and **13**. After one hour under the same conditions, the flux dropped to 0.017 mmol CO₂/m²-s and to about 6×10^{-5} mmol CO₂/m²-s after 24 hours due primarily to changes in the CO₂ driving force across the membrane **150**. In the envisioned application of this system, the decreasing flux is not an issue as the photosynthetic activity of the photoautotrophs will maintain a strong driving force for CO₂ transport. However, significant reduction in external mass transfer resistance will be necessary for practical application of this system.

Example 4

Integrated CO₂ Adsorption and Desorption with CO₂ Delivery

An integrated experiment was used to demonstrate CO₂ adsorption and desorption coupled with CO₂ delivery via a membrane contactor **320**. A packed bed column with of APTES sorbent **110** was used to capture CO₂ from a gaseous stream **100**. The 17.4 mL column was first filled with 0.5 g of glass wool then 1 g of 3 min glass beads **280**. Then 10 g of the APTES sorbent **110** was placed on top of the glass beads **280** and another 1 g of 3 mm glass beads **280** was placed on top of the APTES sorbent **110**.

A 12.0% mol/mol CO₂ (the rest N₂) stream **100** was fed into the column at a rate of 0.05 SCFH (standard cubic feet per hour) (22.39 mL/min). The amount of CO₂ in the exit stream **102** was measured using a quadrupole mass spectrometer and the amount of CO₂ adsorbed was calculated using a breakthrough curve. The amount of CO₂ adsorbed was 1.54 mg as C. The adsorption of CO₂ by the amine sorbent **110** occurred within twenty minutes.

After an hour of flowing gaseous mix of CO₂/N₂, the gas valves were closed and the stripping solution **120** was flowed over the column to remove CO₂ from the APTES sorbent **110**. A stripping solution **120** was prepared by mixing NaOH and NaHCO₃ to produce the necessary pH and DIC levels. The initial DIC concentration in the stripping solution **120** was measured to be 33.76 mg/L. The stripping solution **120** was in contact with the sorbent **110** for 24 hours while 1.5 mL grab samples were used to determine the DIC concentration over time (FIG. **14**). The final DIC concentration was measured to be 37.18 mg/L. The resulting 3.42 mg/L increase in DIC concentration corresponds to stripping 1.37 mg of CO₂ from the sorbent **110** or 88.9% removal.

After 24 hours the flow of the loaded stripping solution **140** was then redirected to the membrane contactor **320**. The receiving water solution **160**, on the permeate side of the membrane contactor **320**, was a CO₂-poor seawater solution **160** with an initial DIC concentration of 24.28 mg/L and a pH of 8.28 used to simulate the algal broth in a photobioreactor. The receiving aqueous solution **160** was made by placing 17.97 g of Instant Ocean® inside a Tedlar® bag reactor. Then 500 mL of boiling deionized water was pumped into the bag to dissolve the Instant Ocean® salts. The DI water was boiled to minimize uptake of ambient CO₂. Afterwards, solution **160** was pumped out of the bag reactor and used for initial measurements leaving a final volume of 400 mL. The synthetic seawater **160** and the stripping solution **120** were in contact with the PDMS membrane **150** for about 24 hours. Grab samples were removed from the synthetic seawater solution **190** to determine the DIC concentration over time (FIG. **15**). The final DIC concentration in the seawater **190** was 25.71 mg/L resulting in a 1.43 mg/L increase in DIC concentration.

The increase in DIC concentration corresponds to 0.57 mg of CO₂ delivered to the synthetic sea water solution **190** from the captured CO₂ APTES sorbent **110**.

In practice the CO₂ in the seawater would be consumed by the photoautotrophs to produce a biofuel. The continuous production and removal of the biofuel provides a nearly continuous CO₂ driving force. This experiment demonstrates a method of delivering CO₂ from gaseous phase to aqueous phase in a form that is consumed by photoautotrophs during photosynthetic processes using a solid sorbent and a gas permeable membrane contactor **320**.

Example 5

Prophetic Example of Economic Modeling

A production target of 6,000 gallons of ethanol per acre per year is over 10 times greater than the productivity of corn-based ethanol. See Luo et al., Life Cycle Energy and Greenhouse Gas Emissions for an Ethanol Production Process Based on Blue-Green Algae. *Environmental Science & Technology* 2010, 44, (22), 8670-8677. This CO₂ demand would require about 2100 mol CO₂ per acre per day. Assuming a CO₂ permeance consistent with elimination of external mass transfer resistance (i.e., 24 GPU) and continuous delivery for 12 hours of daylight each day, the system would require about 80 m² of membrane surface per acre or about 0.013 m² per gal of ethanol produced per year. At \$100 per m² for the full membrane unit cost, the capital investment would be about \$1.3 on this per gal basis. Amortized over 15 years, the contribution to the cost of a gallon of ethanol would be about \$0.09, a cost that would be offset, at least partially, by the cost savings in the CO₂ capture system. In comparison, a \$50/tonne cost for CO₂ capture translates, stoichiometrically, to about \$0.30 per gallon of ethanol. See Solomon et al., IPCC 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, N.Y., USA, 2007.

Equivalents

Those of ordinary skill in the art will recognize, or be able to ascertain, using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims. The invention is embodied in each novel characteristic and each combination of characteristics, which particularly includes every combination of any features which are stated in the claims, even if this feature or this combination of features is not explicitly stated in the claims or in the examples.

What is claimed is:

1. A system for delivery of carbon to a photoautotroph comprising:

- (a) a stream containing CO₂;
- (b) a solid adsorbent comprising materials suitable for CO₂ capture;
- (c) a carbonate-based stripping fluid;
- (d) a device for washing the sorbent, loaded with CO₂ from the stream, with the carbonate stripping fluid, thereby allowing removal of CO₂ from the sorbent and formation of a bicarbonate rich contacting solution;
- (e) a CO₂ selective dense (non-porous) polymer membrane incorporated into a module allowing transfer of CO₂ between the bicarbonate rich contacting solution and a photoautotroph culture medium;
- (f) a baffle disposed on a surface of the CO₂ selective dense (non-porous) polymer membrane; and

(g) a microfiltration membrane which prevents direct contact between the photoautotroph culture medium and the bicarbonate rich contacting solution, wherein the photoautotroph culture medium is enriched with bicarbonate providing carbon for growth of the photoautotroph.

2. The system of claim 1, wherein the CO₂ selective dense (non-porous) polymer membrane comprises a polymer selected from the group consisting of glassy polymers with operating pore sizes smaller than the size of a hydrated sodium cation or a hydrated carbonate or bicarbonate anion and non-porous rubbery polymers.

3. The system of claim 1, wherein the CO₂ selective dense (non-porous) polymer membrane comprises a polymer selected from the group consisting of polydimethylsiloxane, cellulose acetate, polyimides and polyether sulfones.

4. The system of claim 1, wherein the CO₂ permeability of the CO₂ selective dense (non-porous) polymer membrane is approximately 100-10,000 Barrer.

5. The system of claim 1, wherein the CO₂ selective dense (non-porous) polymer membrane comprises polydimethylsiloxane with CO₂ permeability of 3800 Barrer at 35° C.

6. The system of claim 1 wherein the CO₂ selective dense (non-porous) polymer membrane comprises polydimethylsiloxane with CO₂ permeability of 2170 Barrer at 22° C.

7. The system of claim 1, wherein the CO₂ selective dense (non-porous) polymer membrane comprises polydimethylsiloxane with CO₂ gas selectivity of $\alpha_{\text{CO}_2/\text{O}_2}=5.5$ and $\alpha_{\text{CO}_2/\text{N}_2}=10.5$ at 22° C.

8. The system of claim 1, wherein the stream containing CO₂ is air.

9. The system of claim 1, wherein the photoautotroph is an alga.

10. The system of claim 1, wherein the photoautotroph is a cyanobacterium.

11. The system of claim 1, wherein the sorbent is an amine-functionalized polymer or inorganic substrate.

12. The system of claim 1, wherein the sorbent is 3-Aminopropyltriethoxysilane (APTES).

13. The system of claim 1, wherein the stripping solution is a sodium-based carbonate solution.

14. A method for delivering carbon to a photoautotroph comprising:

- (a) providing a stream containing CO₂;
- (b) passing the CO₂ over a solid adsorbent comprising materials suitable for CO₂ capture;
- (c) passing a carbonate-based stripping fluid over the CO₂ loaded sorbent, thereby allowing the removal of CO₂ from the sorbent and formation of a bicarbonate contacting solution;
- (d) utilizing a CO₂ selective dense (non-porous) polymer membrane that allows the transfer of CO₂ between the bicarbonate rich contacting solution and a photoautotroph culture medium, wherein a baffle is disposed on a surface of the CO₂ selective dense (non-porous) polymer membrane; and
- (e) utilizing a microfiltration membrane to prevent direct contact between the photoautotroph culture medium and the bicarbonate rich contacting solution, wherein the photoautotroph culture medium is enriched with bicarbonate providing carbon for growth of the photoautotroph.

15. The method of claim 14, further comprising increasing flow rates of the bicarbonate rich contacting solution and the photoautotroph culture medium across surfaces of the CO₂ selective dense (non-porous) polymer membrane and increasing shear mixing.

16. A system for delivery of carbon dioxide to a photoautotroph comprising:

- (a) a carbon dioxide-adsorbing device comprised of adsorbent particles comprising amine functionality suitable for capture of carbon dioxide; 5
- (b) a stripping device which removes carbon dioxide from the adsorbent particles loaded with carbon dioxide wherein the stripping device comprises a stripping solution comprising carbonate and bicarbonate anions;
- (c) a CO₂ selective dense (non-porous) polymer membrane 10 incorporated into a module allowing transfer of CO₂ between a bicarbonate rich contacting fluid and a photoautotroph culture medium; and
- (d) a baffle disposed on a surface of the CO₂ selective dense (non-porous) polymer membrane. 15

17. The system of claim 16 wherein the stripping device provides a stripping solution with dissolved inorganic carbon (DIC) concentration in the range 270 mg/L to 12,000 mg/L and the photoautotrophic culture medium has an operating DIC range from 0.3 mg/L to 3,000 mg/L. 20

* * * * *